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METAL BONDED TITANIUM DIBORIDE

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FOREWORD

This report, No. 61, was prepared by J. A. Nelson, T. A. Willmore, and D. G. Bennett, at the University of Illinois in the Department of Ceramic Engineering under U. S. Air Force contract No. W33-038 ac-14520. It covers a study of body properties and reactions when combinations of titanium diboride and selected metals were sintered at high temperatures. The technical phases of the contract are administered by the Power Plant Laboratory of the Wright Air Development Center with Mr. B. L. Paris acting as project engineer. It is identified as a project No. 1035 under E. O. No. R-506-67, Ceramic Components for Aircraft Power Plants.

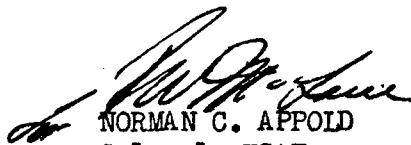
ABSTRACT

Titanium diboride in a finely divided state was combined with thirty percent (by weight) of either powdered iron, cobalt, nickel, chromium, or zirconium and pressed into compacts which were fired in an argon atmosphere at temperatures exceeding the melting point of the added metal. The sintering characteristics of the compacts and the phases present after firing are described. Tests were made for oxidation resistance at 2000°F. The information obtained from this investigation is discussed with a view towards further work regarding the possibilities of using metal bonded titanium diboride in high temperature applications for flight propulsion units.

PUBLICATION REVIEW

The publication of this report does not constitute approval by the Air Force of the findings or the conclusions contained therein. It is published primarily for the exchange and stimulation of ideas.

FOR THE COMMANDING GENERAL:



NORMAN C. APPOLD
Colonel, USAF
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METAL BONDED TITANIUM DIBORIDE

I. INTRODUCTION

The stringent requirements of materials that will give satisfactory service in components of flight propulsion units which are operated at elevated temperatures have been set forth many times^{1,2}. It was the purpose of this investigation to make a study of titanium diboride bonded with one of several metals in order to establish whether such materials show promise for use under the conditions referred to above.

It has been reported³ that when compositions containing boron carbide and titanium carbide plus a bonding metal are subjected to high temperatures the two carbides react to form titanium diboride. The bonding metals also react with boron carbide to form borides. Therefore, it appeared that the more stable compound titanium diboride plus a bonding metal might produce a strong, dense body that would not be subject to disruptive volume changes due to reactions such as those which occurred between boron carbide and titanium carbide. Further, titanium diboride was believed to have some of the desirable properties of each of the carbides.

Compacts of titanium diboride with one of the metals iron, cobalt, nickel, chromium, or zirconium were fired in an argon atmosphere at three different temperatures above the melting point of the bonding metal. Oxidation tests and X-ray and microscopic studies were made on the fired specimens. The results are presented in this report.

The work described herein constitutes the first phase of an overall program on the development of metal bonded titanium diboride. Following investigations will be directed toward obtaining engineering data by means of laboratory and service tests of parts made from these compositions.

II. DISCUSSION OF THE PROBLEM

1. Results of Prior Investigation Directly Related to the Problem

In a preceding investigation,³ combinations of titanium carbide and boron carbide plus various bonding metals were studied in an effort to make a composite material retaining the thermal shock resistance and strength at high temperatures of titanium carbide and having a lower density imparted by the boron carbide. Added thermal shock and impact resistance was expected from the metal bond. However, at elevated temperatures the boron carbide reacted with both the titanium carbide and the

bonding metals; the reaction products being titanium diboride, borides of the bonding metals, and free graphite. The volume increases accompanying these reactions as well as the free graphite produced seriously weakened the fired compositions. Although some of the compositions seemed to have merit, the fired products always included either boron carbide or titanium carbide plus titanium diboride, bonding metal borides, and graphite with the amounts dependent upon the ratio of the carbides in the unfired mixtures.

Aside from varying processing techniques, there appeared to be two approaches to the problem of improving the properties of these types of compositions. In one method, a suitable element would be added to the compositions so as to unite with the free graphite liberated by the reactions. This might be titanium in the case of those compositions high in titanium carbide, boron when the body was predominantly boron carbide, or silicon in either case since it has been reported⁴ not to form compounds with boron up to temperatures in the range of those used in the investigation.

Another way of obtaining compositions with improved properties might be to use titanium diboride as an initial constituent since in many of the compositions it was predominant in the fired products. Because this compound is highly stable, it should not react with most of the metals that would be considered for use as a bonding agent. Work on the latter approach is described herein.

2. Selection and Properties of Materials

Titanium diboride has been reported⁵ to have a simple hexagonal structure with $a = 3.028$, $c = 3.228$, and $\frac{c}{a} = 1.064\text{\AA}$. Its density of 4.52 is low enough to compare favorably with other materials under consideration for high temperature applications in aircraft. Little information is available on the strength, thermal shock resistance and oxidation resistance of titanium diboride but zirconium diboride which is isomorphous with titanium diboride has been reported⁶ to have excellent oxidation resistance. Perhaps a primary factor in the oxidation resistance of borides is that all of their oxidation products are solids. Even though boric oxide melts at low temperatures and tends to volatilize, there is a possibility that in combination with refractory oxides a protective layer will form which acts as a barrier to progressive oxidation. Such a layer formed on borides may be more effective in preventing oxidation than those formed on materials such as carbides or nitrides which have a gas as one of their products of oxidation.

The selection of bonding metals was based on availability, their products of oxidation, and somewhat on the results obtained from metal bonded titanium carbide. It was anticipated that

zirconium might react with titanium diboride, but it was included as a matter of interest. Silicon was given consideration because it might contribute to the oxidation resistance. However, some preliminary work indicated it gave better results when used in conjunction with some of the other metals. This work is being continued as a separate investigation and will be reported as such.

3. Exploratory Tests

The initial tests were made using 80 percent titanium diboride with 20 percent of either iron, cobalt, nickel, or chromium. The titanium diboride was used as received from the producer and was reported to contain 5.09 percent of combined and uncombined carbon. When compacts of the above compositions were fired in argon at temperatures up to 3500°F. the anticipated strength and hardness were not obtained, although the fired specimens were free from cracks and they displayed a slight shrinkage, indicating a tendency toward a good fired structure. Since X-ray studies showed the presence of graphite and some metal boride of the bonding metal, it seemed to be apparent that the carbon content of the titanium diboride was affecting the results. Because of the stability of the titanium diboride, it seemed unlikely that the metal borides were forming from a reaction between the bonding metal and the titanium diboride. Upon further consideration of the carbon content it was reasoned that the combined carbon might be present as boron carbide. In that event the boron carbide would react with the bonding metal to form metal borides. The free carbon would react to a limited extent with iron, cobalt, and nickel and more completely with chromium and zirconium. The free carbon that remained as such would act as a barrier to sintering. Therefore, in order to obtain the best results some method of "tying up" both combined and uncombined carbon in the titanium diboride was sought. The most logical method of doing this seemed to be the addition of titanium which should react with the free carbon to form titanium carbide. It is well known that the proposed metals will effectively bond titanium carbide, so its presence in small amounts should not have any significant effect on the results. If the combined carbon is present as boron carbide the titanium would react with it to form titanium diboride and additional titanium carbide. Thus the remaining reaction products should be titanium diboride and titanium carbides, either of which should be readily bound by the added metals.

Calculations based on the analysis of the titanium diboride were made to determine how much titanium should be added to react with the free and combined carbon (as B_4C) in the titanium diboride. This amount of titanium plus a small excess was added to the metal bonded titanium diboride compositions and a significant improvement in results was obtained.

There is also a possibility that bonding metal borides were formed in the initial tests because of an excess of boron in the titanium boride or the presence of another titanium boride phase higher in boron. Another phase has been reported⁷ in which x is approximately equal to 10 in the formula TiB_x . However, such conditions were not indicated by the chemical analysis furnished by the supplier, and if such were the case the added titanium would probably react to form additional titanium diboride as the end product.

4. Procedures Adopted

In one group of specimens the titanium diboride, titanium, and bonding metal were all mixed together and the resulting compacts fired in one operation. It was found, however, that reactions involving the titanium led to a less dense fired structure than expected. In another group of specimens the titanium diboride and titanium only were mixed and subjected to a reaction fire at 3400°F. This material was ground and mixed with the bonding metal, after which compacts of the mixture were refired. Somewhat better results were obtained. Even though a second lot of titanium diboride with lower carbon content (1.29%) was received, titanium additions were made to all bodies. In future studies of these compositions the use of titanium might be eliminated providing a pure grade of titanium diboride could be obtained.

III. EXPERIMENTAL DETAILS

The titanium diboride and metal powders used in this investigation were obtained from commercial sources*. As received, the titanium diboride would all pass a 325 mesh screen, but it was ground finer in a five inch diameter steel mill (using steel balls) which was rotated for 110,000 revolutions. The iron picked up from the milling operation was removed by leaching in a 1:1 solution of 99.5% acetic acid. Previous attempts to remove iron contamination by leaching in hydrochloric acid resulted in some attack on the titanium diboride. After the titanium diboride had been filtered and washed in distilled water until no test for iron was obtained, it was dried, washed in methanol, and passed through a 325 mesh screen. Particle sizes of the titanium diboride, as obtained with the Andreasen Pipette method, are shown in Table 1. The metals were used as received and would pass a 325 mesh screen.

* TiB_2 from Norton Co.; Cr, Co, Ti from A. D. MacKay, Inc.; Zr from Metal Hydrides Co.; Ni from Metals Disintegrating Co.; Fe from General Aniline & Film Corp.

Table 1

Particle Size Distribution of the Titanium Diboride

<u>Particle Size Range in Microns</u>	<u>Percent of the Total (By Weight)</u>
Greater than 30	2
30 - 20	15
20 - 10	41
10 - 5	17
5 and finer	25

Analyses of the titanium diboride as furnished by their producer are given in Table 2. Lot No. 1 was used only in preliminary experiments and all of the compositions described in this report were made from lot No. 2.

Table 2

Chemical Composition of the Titanium Diboride

	<u>Lot No. 1</u>	<u>Lot No. 2</u>
Boron	30.87	30.94
Titanium	62.79	66.35
Total Carbon	5.06	1.29
Free Carbon	4.17	.78

The titanium diboride and metals were mixed in an agate mortar. Benzene was added to the materials to make a slurry and mixing continued while the benzene evaporated. No binder or lubricant was added. Specimens 1/2 in. in diameter and approximately 3/8 in. high were formed by pressing the mixtures in a hardened steel mold at 50,000 psi. These specimens were then repressed hydrostatically at 80,000 psi. The above procedure was followed to make one series of specimens which included all compositions.

In another series of specimens the titanium diboride was initially mixed with only the titanium. This mixture was pressed at 50,000 psi in a steel mold and the resulting compacts fired at 3400°F. The specimens from this reaction fire were then crushed, passed through a 325 mesh screen, and mixed with one of the bonding metals. Compacts were made from these mixtures by pressing them at 50,000 psi in a steel mold. Specimens made in this manner were designated by the letter "A" in their composition number. A micrometer was used to measure the diameter and height of all specimens.

The experimental bodies are listed in Table 3.

Table 3
Experimental Compositions

<u>Body No.</u>	<u>Bonding Metal</u>	<u>Percent by Weight</u>	
		<u>Titanium</u>	<u>Titanium Diboride</u>
T-2	30 Fe	10	60
T-3	30 Zr	10	60
T-4	30 Co	10	60
T-5	30 Ni	10	60
T-6	30 Cr	10	60

The specimens were fired in a tungsten resistance furnace which is described in University of Illinois, Department of Ceramic Engineering Report No. 56, Section III. In all cases an argon atmosphere was employed. The specimens were brought up to temperature (see Table 4) in about one hour. After a one-half hour soaking period, the power was turned off and they were allowed to cool with the furnace.

The fired specimens were measured and sawed into two parts with a diamond cut off wheel. Density determinations were made on one part by obtaining the dry weight and the suspended saturated weight in distilled water. These same pieces were then mounted in lucite in preparation for polishing. The other half of each specimen was used for oxidation tests.

In preparing the specimens for microscopic examination they were first ground on a cast iron lap with 100 mesh silicon carbide. This was followed by two stages of grinding with 500 grit and 800 grit boron carbide on a cast iron lap. They were then transferred to a lap wheel made from fine grain maple wood. A medium fine diamond finishing compound* suspended in spindle oil was applied to the wheel. A second maple lap wheel employing extra fine diamond finishing compound suspended in kerosene was also used. A felt covered wheel with rouge was used for a brief, final polishing.

Oxidation tests were made in a Globar furnace held at 2000°F. The specimens were set on an insulating brick which was placed in the furnace while it was at temperature. Pieces of platinum foil were placed under the specimens so they did not come in contact with the insulating brick. At intervals of 2, 4, 8, 24, 96 and 200 hours the specimens were taken from the furnace, allowed to cool, and weighed on an analytical balance to record the gain in weight.

One specimen from each composition was fired at the temperatures indicated in Table 4, and crushed to pass a 200 mesh screen. The resulting powders were X-rayed using a Norelco X-ray spectrometer with iron radiation.

* Diamond finishing compound from Carborundum Company.

Table 4

Some Fired Properties of Titanium Diboride
Bodies Composed of 60% TiB₂ and 10% Ti plus
30% of the Binder Metal Indicated.

<u>Body No.</u>	<u>Binder Metal</u>	<u>Specimen No.</u>	<u>Firing</u> <u>Temperature</u> <u>°F.</u>	<u>Percent</u> <u>Shrinkage</u>	<u>Density</u>
T-2	Fe	1	3050	3.93	4.26
"	"	2	3250	6.85	4.51
"	"	3	3450	9.17	4.49
"	"	4	3250	Crushed for X-ray studies	
"	"	T-2A	3250	8.11	4.60
T-3	Zr	1	3500	No change	3.77
"	"	2	3700	3.11	3.97
"	"	3	3500	Crushed for X-ray studies	
"	"	T-3A	3600	No change	3.66
T-4	Co	1	2975	6.20	4.66
"	"	2	3175	8.68	4.84
"	"	3	3375	10.15	5.00
"	"	4	3200	Crushed for X-ray studies	
"	"	T-4A	3270	11.45	5.00
T-5	Ni	1	2900	2.47	4.21
"	"	2	3100	4.53	4.44
"	"	3	3300	8.88	4.81
"	"	4	3100	Crushed for X-ray studies	
"	"	T-5A	3200	9.68	4.88
T-6	Cr	1	3200	3.50	4.05
"	"	2	3400	6.61	4.29
"	"	3	3600	7.41	4.33
"	"	4	3400	Crushed for X-ray studies	
"	"	T-6A	3500	7.37	4.39

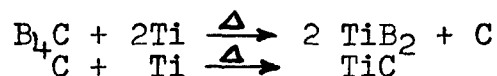
IV. RESULTS AND DISCUSSION

1. Sintering Characteristics and Densities of the Fired Specimens

The firing shrinkage and density for all specimens is shown in Table 4. When iron, cobalt, nickel, or chromium was used as the bonding metal, hard and strong bodies were developed that were free from cracks and metallic in appearance. All of these compositions displayed a certain amount of shrinkage. The specimens containing zirconium were easily sawed with a silicon carbide cut off wheel indicating that they were not nearly as hard as those bonded with the other metals which required a diamond cut off wheel to cut them.

Titanium diboride has a theoretical density of 4.52. Therefore, pure titanium diboride plus the bonding metals used in this investigation would have a theoretical density somewhat higher. However, the titanium additions and its reaction with impurities complicated the calculation of theoretical densities for the compositions studied in this investigation. A composition containing seventy percent pure titanium diboride and thirty percent of either cobalt or nickel would have a theoretical density of 5.31 assuming a mechanical mixture of the constituents. The densities of the cobalt and nickel specimens in this investigation ranged between 4.21 and 5.00.

Slightly higher densities were obtained when the titanium diboride and titanium were pre-reacted at 3400°F. It was believed that this fire caused the following reactions to take place between the titanium and impurities:



Thus during the subsequent fire when the bonding metal was added, the impurities should be "tied up" and there should not be chemical reactions with associated changes in volumes. Even higher densities should be obtained if the specimens from the pre-reaction fire were ground finer than those were in this investigation.

The relatively low density of those specimens containing zirconium was probably due to chemical reactions involving both zirconium and titanium diboride.

2. X-Ray Studies

X-ray data obtained from patterns of the fired specimens are presented in Table 5. The "d" values, relative intensities, and elements or compounds indicated are given for each body type.

Table 5

X-Ray Data

Body No. T-2 (Fe Bonded)			Body No. T-4 (Co Bonded)			Body No. T-5 (Ni Bonded)		
Element Relative or Compound		Element Indicated	Element Relative or Compound		Element Indicated	Element Relative or Compound		Element Indicated
"d"	Intensity		"d"	Intensity		"d"	Intensity	
3.24	1.5	TiB ₂	3.24	1.5	TiB ₂	3.24	2.0	TiB ₂
2.63	4.0	TiB ₂	2.63	4.0	TiB ₂	2.63	4.0	TiB ₂
2.47	.7	TiC	2.47	1.0	TiC	2.47	.5	TiC
-	-	-	2.37	1.0	Ti	2.37	1.0	Ti
2.25	.5	Ti	2.25	.5	Ti	2.25	.5	Ti
-	-	-	2.16	2.0	TiC	2.16	2.0	TiC
2.14	2.0	TiO	2.14	2.0	TiO	2.14	2.0	TiO
2.13	2.0	TiO	-	-	-	-	-	-
2.04	10.0	TiB ₂ and Fe	2.04	10.0	TiB ₂ and Co	2.04	10.0	TiB ₂ and Ni
-	-	-	1.87	.7	-	1.87	.2	-
-	-	-	1.79	1.0	Co	1.79	1.0	Ni
1.64	.2	-	-	-	-	-	-	-
1.62	.2	TiB ₂	1.62	.2	TiB ₂	1.62	.2	TiB ₂
1.54	.5	TiC	-	-	-	-	-	-
1.52	2.0	TiB ₂	1.52	2.0	TiB ₂	1.52	2.0	TiB ₂ and TiC
1.44	.7	Fe	-	-	-	-	-	-
1.38	2.0	TiB ₂	1.38	1.5	TiB ₂	1.38	1.0	TiB ₂

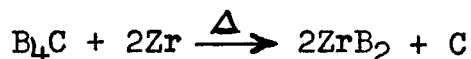
Table 5 (continued)

X-Ray Data

Body No. T-3 (Zr Bonded)			Body No. 6 (Cr Bonded)			1:6 Ti to TiB ₂ (by weight) Fired at 3400°F.		
Element Relative or Compound Indicated			Element Relative or Compound Indicated			Element Relative or Compound Indicated		
"d"	Intensity		"d"	Intensity		"d"	Intensity	
3.24	2.0	TiB ₂	3.24	2.0	TiB ₂	3.24	2.0	TiB ₂
3.16	.7	-	-	-	-	-	-	-
2.93	2.5	ZrO ₂	-	-	-	-	-	-
2.67	6.0	ZrC	-	-	-	-	-	-
2.63	5.5	TiB ₂	2.63	4.0	TiB ₂	2.63	6.0	TiB ₂
2.53	4.0	Ti	-	-	-	-	-	-
-	-	-	2.51	1.0	-	-	-	-
-	-	-	2.47	1.5	TiC	2.47	1.0	TiC
-	-	-	2.36	.5	Ti	-	-	-
2.31	6.0	ZrC	-	-	-	-	-	-
2.22	5.0	Ti	2.25	.5	Ti	-	-	-
2.17	1.0	ZrB ₂	-	-	-	-	-	-
-	-	-	-	-	-	-	-	-
-	-	-	2.16	3.0	TiC	2.16	1.0	TiC
-	-	-	2.14	3.0	TiO	2.14	2.0	TiO
2.04	10.0	TiB ₂	2.04	10.0	TiB ₂ and Cr	2.04	10.0	TiB ₂
-	-	-	1.99	1.0	-	-	-	-
1.71	1.0	Ti	-	-	-	-	-	-
1.64	3.0	ZrC	-	-	-	-	-	-
1.62	.5	TiB ₂	1.62	1.0	TiB ₂	1.62	1.0	TiB ₂
1.55	.8	-	-	-	-	-	-	-
1.52	1.5	TiB ₂	1.52	2.0	TiB ₂ and TiC	1.52	2.5	TiB ₂ and TiC
1.44	1.5	ZrC	-	-	-	-	-	-
1.38	3.0	TiB ₂	1.38	1.5	TiB ₂	1.38	2.5	TiB ₂

Fired specimens bonded with iron, cobalt, nickel or chromium were found to contain titanium diboride, bonding metal, titanium carbide, titanium mono-oxide (TiO) and titanium. In every case strong peaks were obtained for titanium diboride which has its most intense peak occurring at 2.04\AA . Since the most intense peaks for iron, cobalt, nickel, and chromium also occur very close to 2.04\AA , the peaks for these metals and titanium diboride overlapped thus producing one strong peak. However, the bonding metals were known to remain as such in the fired specimens because some of their minor peaks appeared and no other compound of these metals was found as a principal constituent. Their presence was also established by microscopic studies. The failure to detect any borides of the bonding metals indicated that titanium diboride was stable with respect to them and that the added titanium had reacted with the boron carbide believed to have been present in the original titanium diboride. The presence of titanium carbide indicated that the titanium added to the specimens was effectively "tying up" the free carbon. Titanium carbide peaks were weak in all cases since it was present in relatively small amounts. Weak peaks were also found for TiO which was probably formed during firing because of some oxygen in the atmosphere or occluded gases in the raw materials. If TiO was present in the raw materials, it was not detected when they were X-rayed. Some low intensity peaks were thought to have arisen from titanium. This is possible since an excess beyond that required to react with impurities was added.

The specimens containing zirconium as a bonding metal were found to have titanium diboride, zirconium carbide, zirconium diboride, titanium, and some zirconium oxide as fired products. There was probably also some solid solution of zirconium diboride and titanium diboride. In these compositions the zirconium served to "tie up" the free carbon since it has a greater affinity for carbon than does titanium. The remainder of the zirconium that did not react with carbon was apparently converted to the boride. Zirconium diboride may have been formed in two ways. First, if initially there was some boron carbide present the following reaction would occur:



Secondly, it is likely that zirconium diboride was formed by zirconium displacing titanium in some of the titanium diboride. Actually, the X-ray patterns gave only weak evidence of zirconium diboride, but this may have been because part of it entered into solid solution with titanium diboride. It has been shown^o that zirconium diboride and titanium diboride form complete solid solutions.

There is also a possibility that a small amount of titanium carbide was produced which formed solid solutions with the zirconium carbide. Some of the zirconium carbide peaks seem to have shifted slightly.

It should be noted that the reaction products described are the result of the particular firing treatment employed in this investigation. If heated to equilibrium conditions, the end products would be different, at least in the amounts formed, and especially when the principal constituents entered into reaction such as occurred in the specimens containing zirconium.

3. Microscopic Examination

Figures 1 through 5 show all compositions at 100 magnification so they can be compared as to their number of internal voids. With the exception of those specimens containing zirconium, the least number of voids were displayed by the specimens which were made by pre-reacting the titanium diboride and titanium, crushing this material, and refiring compacts made from it and the bonding metal. The specimens fired in one operation, but at several different temperatures, exhibited the least number of voids at the highest temperature of firing. However, increased firing time would probably improve the results at lower temperatures, particularly when impurities such as those described are present. In subsequent work to evaluate these bodies an effort will be made to decrease the porosity by using a purer titanium diboride and by improving processing techniques.

The microstructures of all compositions are shown in Figures 6 through 10. In all specimens with the exception of those containing zirconium the photomicrographs revealed a marked tendency of the titanium diboride for grain growth. This is particularly well illustrated by the unetched, iron bonded specimen shown in Figure 6(b). In some areas the titanium diboride grains have grown so as to form a continuous boride skeleton which is filled in with the iron.

In several photomicrographs the individual grains of titanium diboride appeared to contain flaws or voids. This was more noticeable for those specimens which were etched and may have been due in part to attack of the boride by the etching agent. Possibly, the titanium diboride particles in the unetched specimens seemed to contain less voids because they were filled in by a thin layer of metal which was "smeared" over the surface during the polishing. Upon etching, some of this metal might have been removed thus presenting a truer picture of the boride grain surface. In any event, the structure of the individual boride grains should be studied and the effect on body properties taken into consideration when physical tests are undertaken. If it is

indicated that defects within the individual boride grains are lowering strength values, an improvement might be realized from finer grinding or varying the firing techniques to promote recrystallization.

In those compositions that did not contain zirconium a phase was found which was identified as TiO. Under the microscope this phase was brassy in appearance, which is characteristic of either TiO or TiN. The X-ray analysis indicated it was TiO. Although the TiO was present in relatively minor amounts, it was uniformly distributed throughout the specimens. For this reason it appeared that the oxygen was most likely introduced into the specimens with the raw materials and by entrapped air when the compacts were pressed. If the main source of the oxygen had been derived from the furnace atmosphere it would seem that greater concentrations of TiO would have been found near the surface of the specimens.

It was found from the X-ray analysis that the carbon in these specimens had reacted with titanium to form titanium carbide. However, the titanium carbide phase was not readily distinguished under the microscope. Calculations indicated that approximately 5 percent (by volume) of the fired compositions was titanium carbide. Perhaps the carbon was so finely dispersed that only very minute titanium carbide crystals formed which were not resolved under the microscope. Experimentation with other etching techniques may also aid in bringing out this phase.

Photomicrographs of the compositions containing zirconium (Fig. 10) do not effectively differentiate between the various phases that X-ray studies indicated were present. This may be attributed partially to difficulty in polishing these highly porous specimens. The dark grey areas, although not positively identified, are thought to be an oxide of zirconium. In these specimens the zirconium probably combined with any oxygen present whereas in the others titanium acted as an oxygen "getter." More of the phase believed to be an oxide of zirconium appeared near the surface of the specimens, suggesting that in these porous bodies the source of some of the oxygen may have been the furnace atmosphere. Fig. 10(b) shows an area near the outer surface of the specimen.

4. Oxidation Tests:

The gain in weight of specimens heated at 2000°F. for time periods up to 200 hours is shown by the curves in Fig. 11. Under the conditions of these tests, the best oxidation resistance was displayed by the specimens bonded with either chromium or nickel. None of the specimens containing iron, cobalt, or

zirconium were considered worthy of further testing after 24 hours. At the end of this time period they had oxidized to the point where they had lost their shape or cracked.

A tightly adhering protective oxide layer was formed on the surface of the bodies that were bonded with chromium or nickel. Photomicrographs showing this layer and the interface between it and the original specimen are presented in Figs. 12 and 13. The oxide layer is composed of the oxides of titanium, boron, and either chromium or nickel. Apparently the oxides were in the proper ratio so that they did not become fluid at 2000°F., but yet fused sufficiently to form a protective barrier against progressive oxidation. Once a continuous protective coating has been formed oxidation may continue, but usually at a much slower rate, depending upon diffusion of oxygen through that coating.

The specimens containing iron and cobalt formed oxides which combined to produce a coating that was somewhat fluid at 2000°F. As a result the continuity of the protective layer was lost and oxidation progressed to such an extent within 24 hours that these compositions were not considered satisfactory for service at 2000°F. It is possible that at temperatures a few hundred degrees lower, the coatings on these specimens would be sufficiently viscous to give protection from oxidation.

The specimens containing zirconium were highly porous. When they were subjected to the oxidation test, they did not develop an oxide layer that fused to seal off the pores. Therefore, oxygen penetrated into the specimens until they were almost entirely converted to oxides and they cracked from the volume changes.

Such unfavorable preliminary oxidation tests are not a basis for the elimination of iron and cobalt bonded titanium diboride compositions. The oxidation resistance is primarily dependent upon the kind of oxides and by the relative amounts of those oxides which are formed in a protective layer at the surface. Therefore, the amounts of the constituents in these compositions may be altered so their oxides will combine in proportions to produce less fluidity of the protective coating.

From the standpoint of oxidation alone it is indicated that an investigation in which the oxides were combined in various proportions and studied at different temperatures might be helpful in determining compositions that would develop the best protective layers when oxidized. Based on such a study, the initial constituents of the bodies would be combined so their oxidation products would create the desired coating. However, it is likely that under such circumstances the best composition

for oxidation resistance might not be the most desirable with respect to other properties such as strength, thermal shock resistance, and density. All properties must be considered in their order of importance, but a basis for formulating oxidation resistant compositions might be established by beginning with a study of the oxides produced.

V. SUMMARY

Titanium diboride can be bonded with 30 percent (by weight) of iron, cobalt, nickel or chromium to form hard, dense bodies. No reaction was detected between titanium diboride and any of the above metals when the specimens were fired at temperatures up to 600°F. above the melting point of the metal. The titanium diboride used in this investigation contained impurities which were carbon and probably boron carbide. To minimize the effect of the impurities, ten percent titanium was added to the compositions. The titanium reacted with free carbon to form titanium carbide and with the boron carbide to form titanium diboride and titanium carbide. Bodies of somewhat higher density were produced when the titanium diboride and titanium was pre-reacted at 3400°F. than when the titanium diboride, titanium, and bonding metal were fired in one operation.

When zirconium was used as a bonding metal, bodies were produced which were relatively porous and weak. In these compositions the zirconium rather than the titanium reacted with the impurities in the titanium diboride to form zirconium carbide and zirconium diboride. Some zirconium diboride was probably formed by displacement of titanium in the titanium diboride. Most likely some of the zirconium diboride entered into solid solution with titanium diboride.

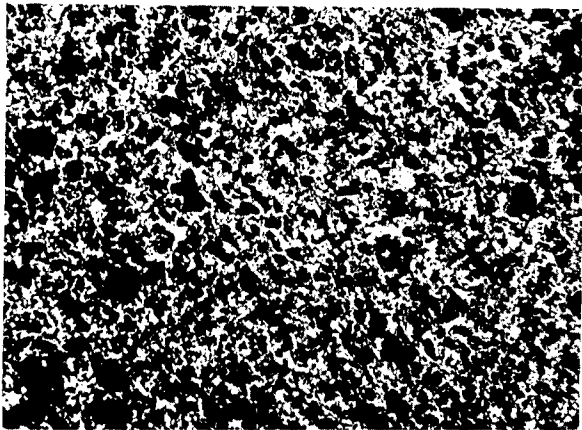
Photomicrographs at low magnification demonstrated that in general, the specimens contained an appreciable number of internal voids. Appropriate changes in processing techniques are expected to create denser bodies. At higher magnifications, photomicrographs illustrated voids within the individual grains of titanium diboride, grain growth of the titanium diboride, the distribution of the metallic phase, and other phases such as titanium mono-oxide which resulted from impurities which were present in the raw materials or were introduced during processing.

Oxidation tests at 2000°F. showed the specimens with 30 percent of either chromium or nickel to have the best oxidation resistance. After 200 hours at 2000°F. they were structurally sound although a relatively thick oxide layer was developed on the surface. The specimens containing iron, cobalt, or zirconium did not develop an effective protective coating and tests on them were discontinued after 24 hours.

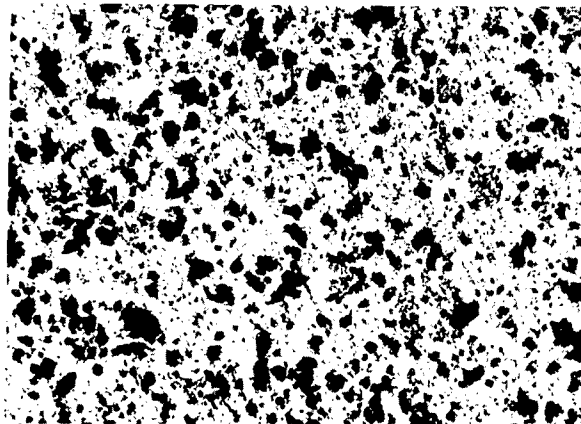
This investigation should logically be followed by additional work to improve and evaluate by physical testing the compositions containing titanium diboride and either chromium or nickel. Further work is also warranted on bodies employing iron or cobalt as a bond for titanium diboride, but particular emphasis should be placed on varying their compositions to improve their oxidation resistance. Rather than to attempt bonding titanium diboride with zirconium, it seems more advisable to use zirconium diboride or a solid solution of zirconium diboride and titanium diboride as a starting component in such bodies and to employ other metals as a bond.

VI. REFERENCES

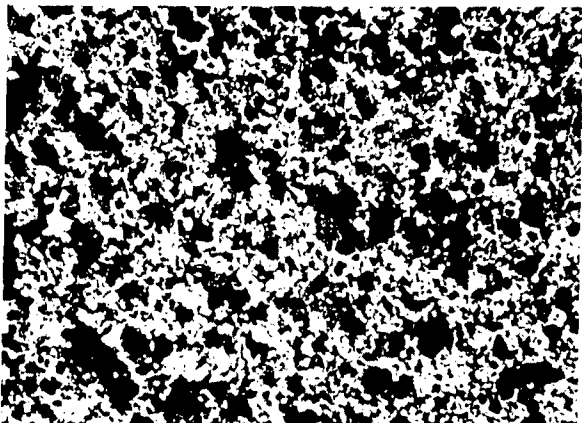
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2. James J. Gangler, Chester F. Robards, and James E. McNutt, "Physical Properties at Elevated Temperature of Seven Hot-Pressed Ceramics," NACA TN 1911, July 1949.
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8. "Cemented Borides," Part III, Progress Report, Contract N6-ONR-256, American Electro Metal Corporation, 30-35, March 1 - October 1, 1951.



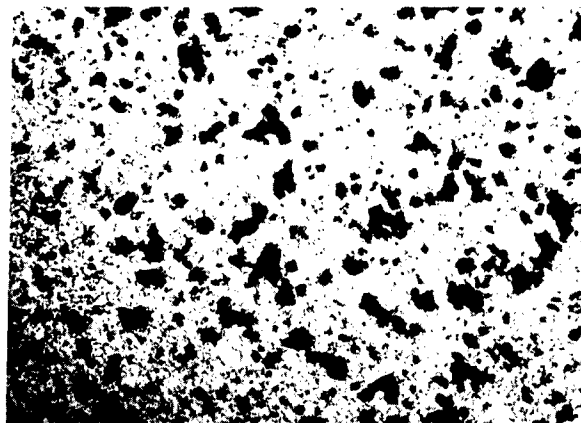
(a) Fired at 3050°F.
Density, 4.26 gms/cm³



(b) Fired at 3250°F.
Density, 4.51 gms/cm³

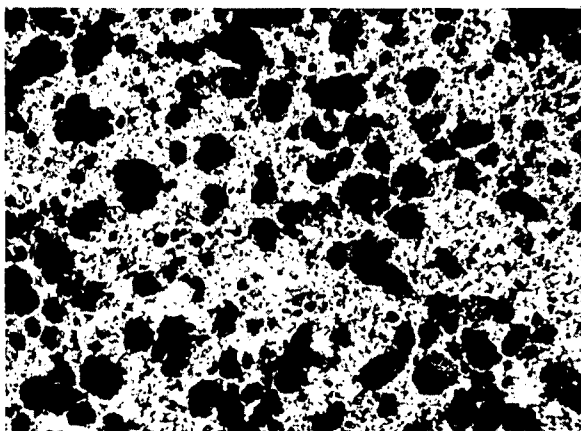


(c) Fired at 3450°F.
Density, 4.49 gms/cm³

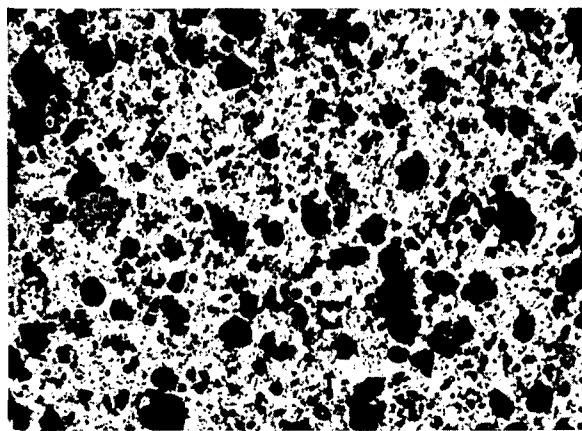


(d) Fired at 3250°F.
Density, 4.60 gms/cm³
(TiB₂ and Ti pre-reacted
at 3400°F.)

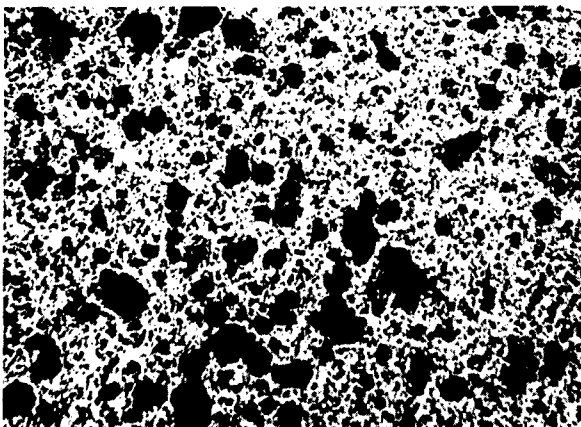
Fig. 1. Photomicrographs showing the fired porosity of specimens made from titanium diboride plus 10 percent titanium and 30 percent iron. X100.



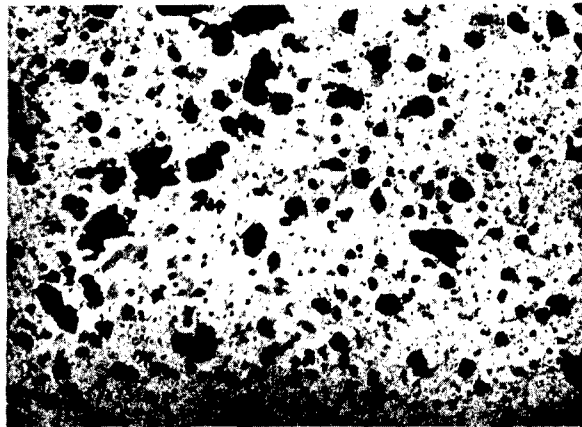
(a) Fired at 2975°F.
Density, 4.66 gms/cm³



(b) Fired at 3175°F.
Density, 4.84 gms/cm³

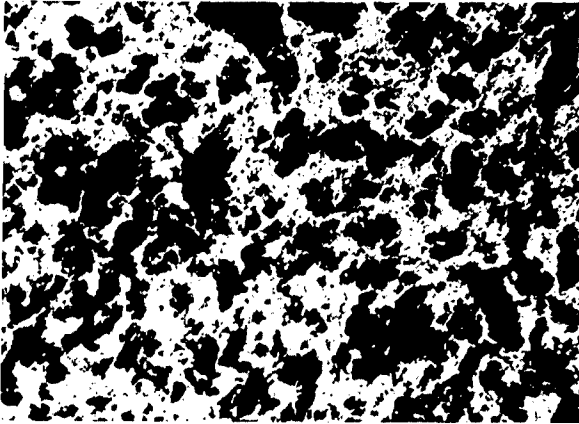


(c) Fired at 3375°F.
Density, 5.00 gms/cm³

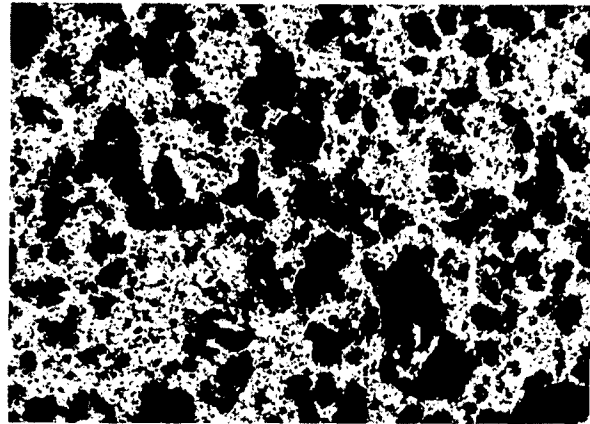


(d) Fired at 3270°F.
Density, 5.00 gms/cm³
(TiB₂ and Ti pre-reacted
at 3400°F.)

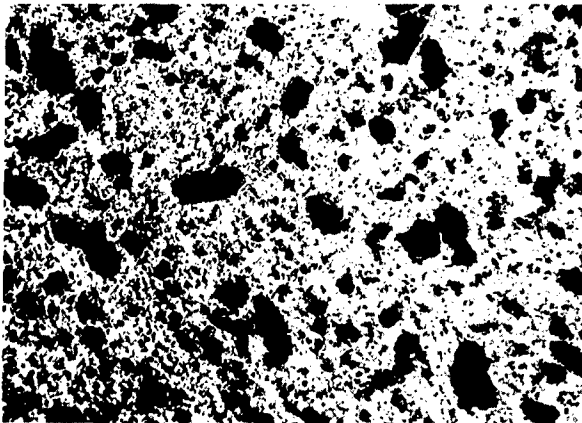
Fig. 2. Photomicrographs showing the fired porosity of specimens made from titanium diboride plus 10 percent titanium and 30 percent cobalt. X100.



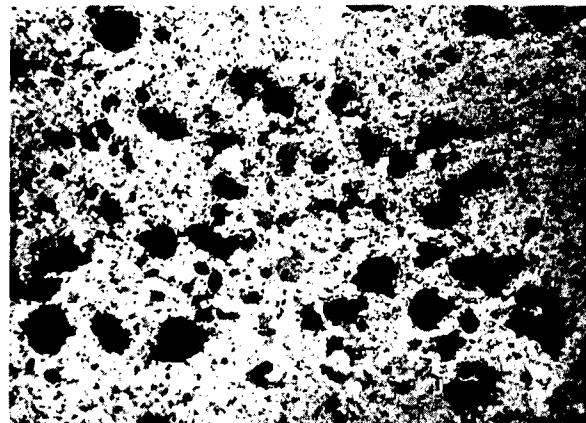
(a) Fired at 2900°F.
Density, 4.21 gms/cm³



(b) Fired at 3100°F.
Density, 4.44 gms/cm³

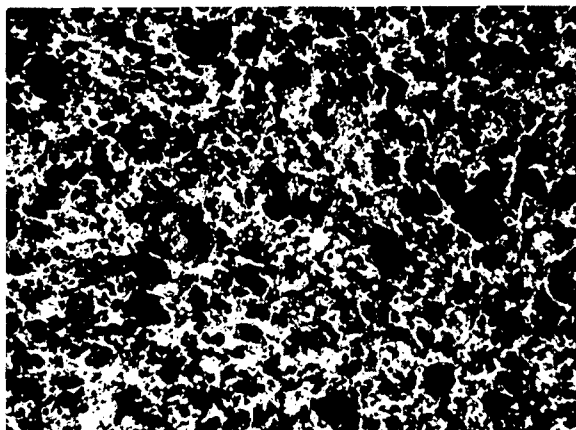


(c) Fired at 3300°F.
Density, 4.81 gms/cm³

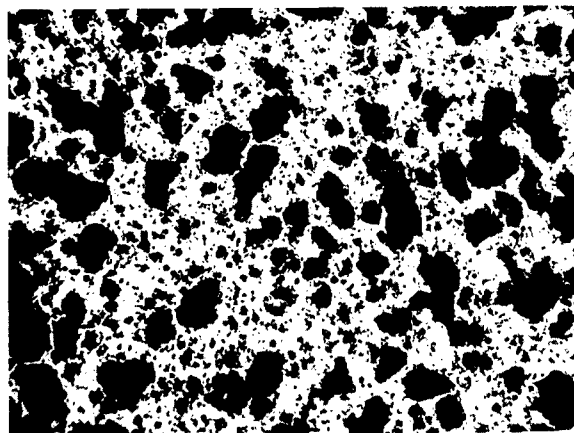


(d) Fired at 3200°F.
Density, 4.88 gms/cm³
(TiB₂ and Ti pre-reacted
at 3400°F.)

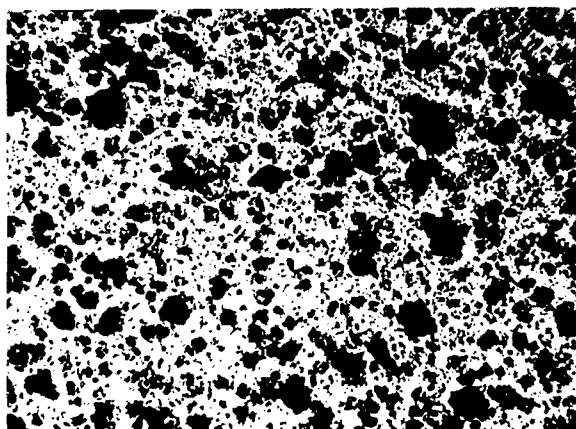
Fig. 3. Photomicrographs showing the fired porosity of specimens made from titanium diboride plus 10 percent titanium and 30 percent nickel. X100.



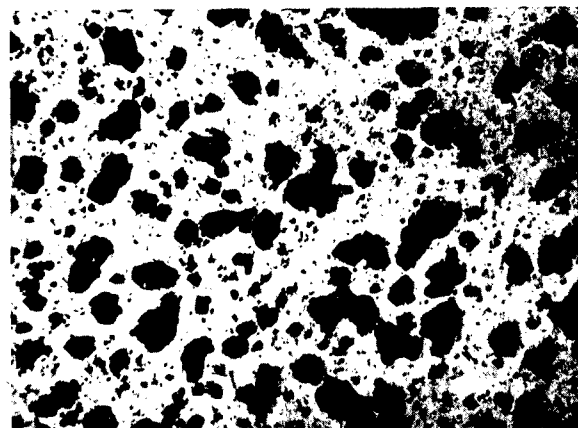
(a) Fired at 3200°F.
Density, 4.05 gms/cm³



(b) Fired at 3400°F.
Density, 4.29 gms/cm³

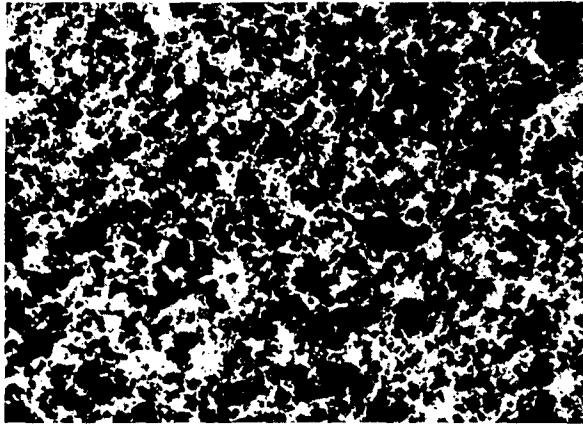


(c) Fired at 3600°F.
Density, 4.33 gms/cm³

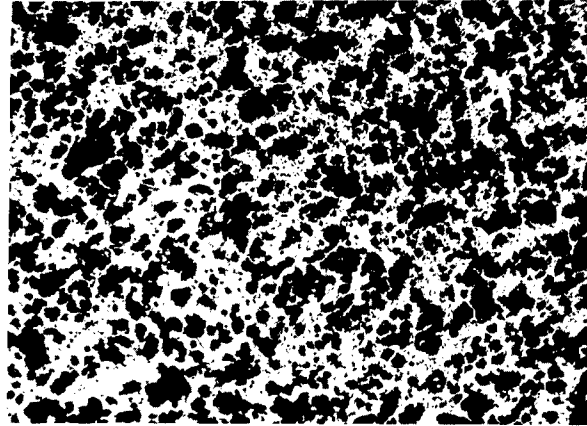


(d) Fired at 3500°F.
Density, 4.39 gms/cm³
(TiB₂ and Ti pre-reacted
at 3400°F.)

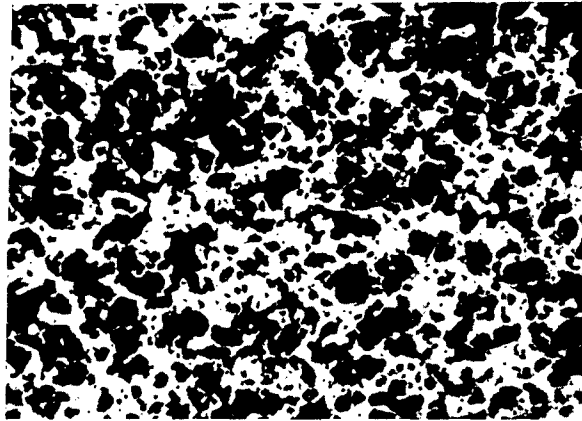
Fig. 4. Photomicrographs showing the fired porosity of specimens made from titanium diboride plus 10 percent titanium and 30 percent chromium. X100.



(a) Fired at 3500°F.
Density, 3.77 gms/cm³

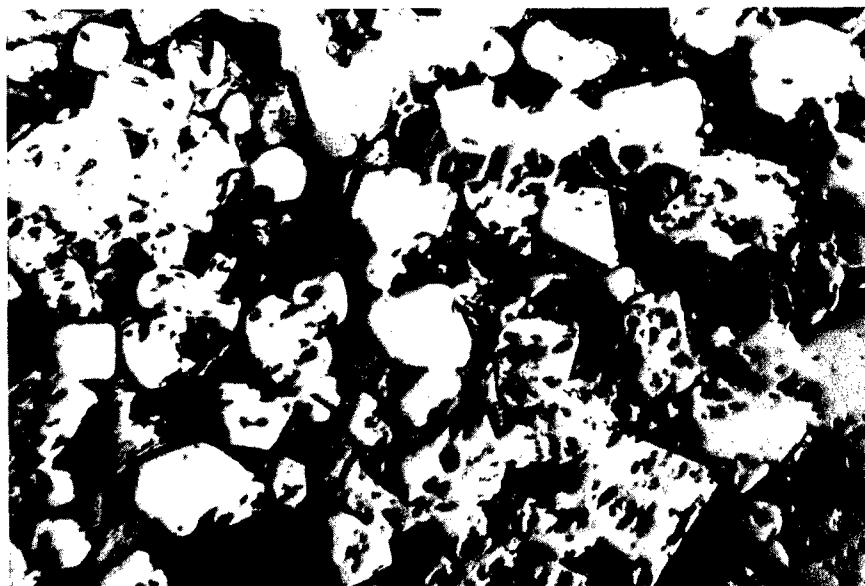


(b) Fired at 3700°F.
Density, 3.97 gms/cm³

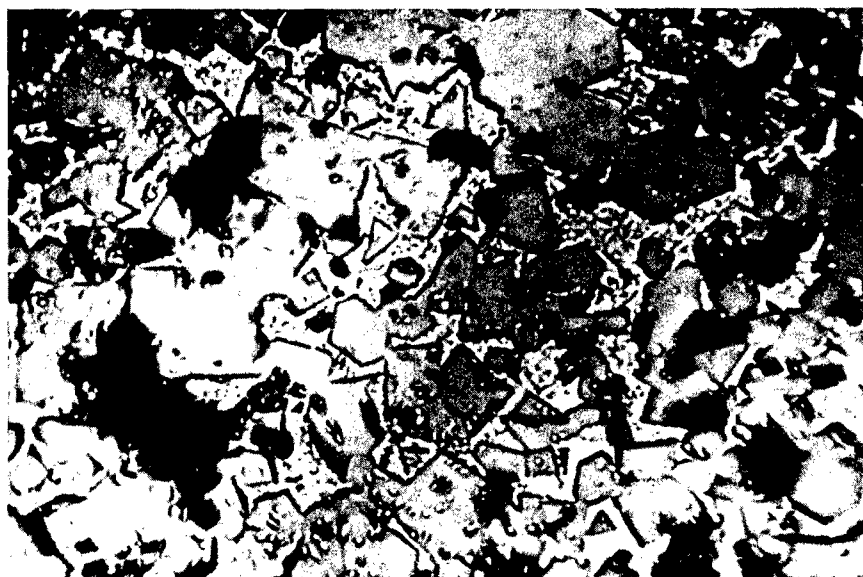


(c) Fired at 3600°F/
Density, 3.66 gms/cm³
(TiB₂ and Ti pre-reacted
at 3400°F.)

Fig. 5. Photomicrographs showing the fired porosity of specimens made from titanium diboride plus 10 percent titanium and 30 percent zirconium. X100.

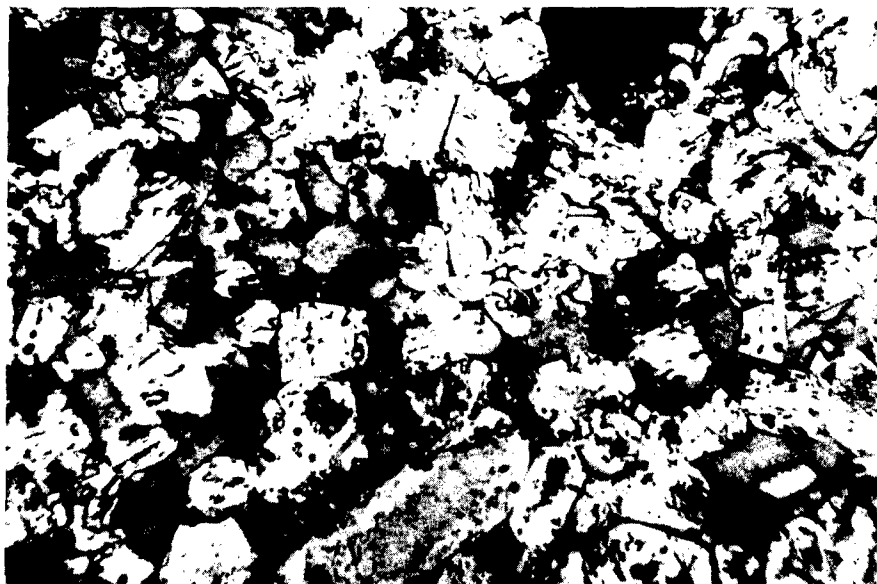


(a) Fired at 3450°F. Light, angular grains are TiB_2 . Pits or voids in the individual grains might be characteristic of the material used or may have been caused by etching. Etched 15 sec. in nital.

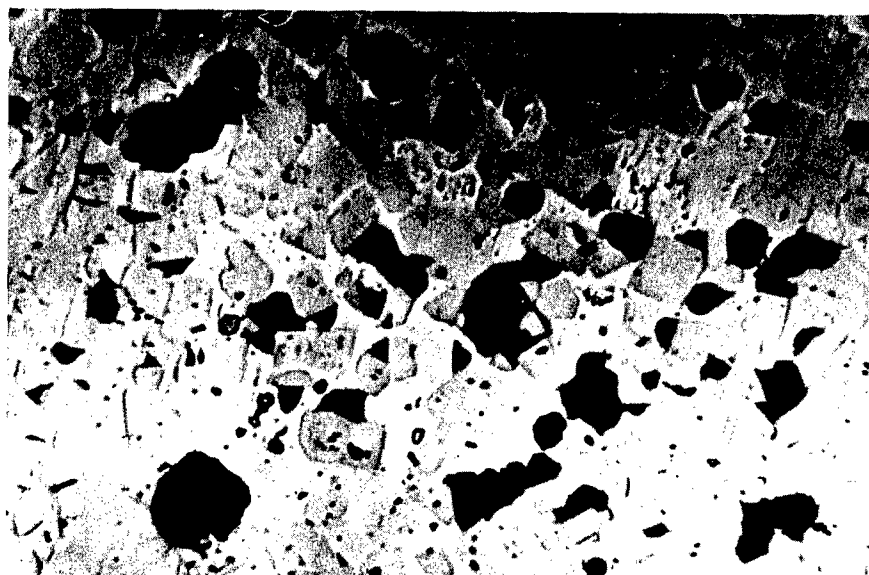


(b) Fired at 3250°F. (Ti and TiB_2 pre-reacted at 3400°F.) Light grey, angular areas are TiB_2 which shows considerable grain growth. The light areas between the grains are iron. Unetched.

Fig. 6. Microstructures of specimens made from titanium diboride plus 10 percent titanium and 30 percent iron. X 1200



(a) Fired at 3175°F. Etched 5 min. in a solution consisting of 4 parts 48% HF, plus 2 parts conc. HNO_3 , plus 94 parts methanol.



(b) Fired at 3270°F. (Ti and TiB_2 pre-reacted at 3400°F.) Dark grey areas in center of photo appear brassy under the microscope and are identified as TiO .

Fig. 7. Microstructures of specimens made from titanium diboride plus 10 percent titanium and 30 percent cobalt. X 1000

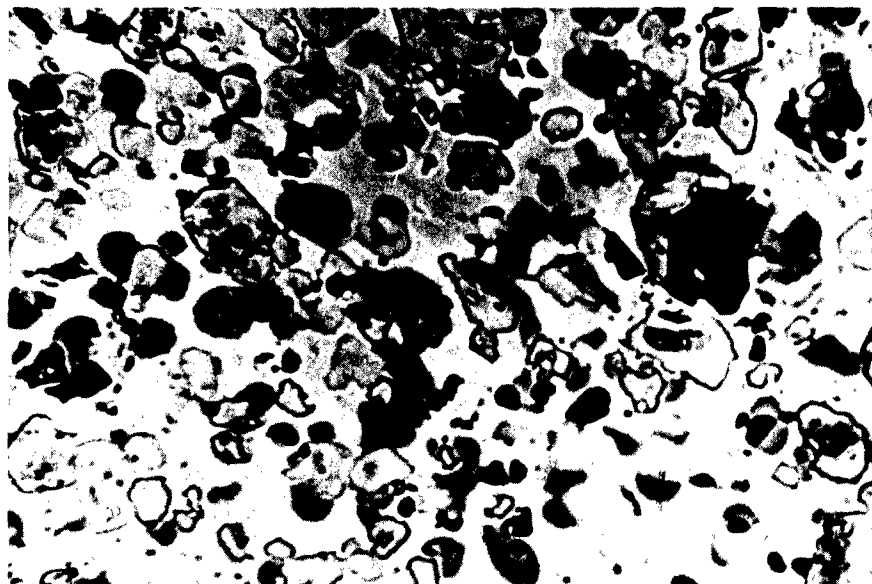


(a) Fired at 3300°F. Etched 1 min. in a solution consisting of 4 parts 48% HF, plus 2 parts conc. HNO₃, plus 94 parts methanol.



(b) Fired at 3200°F. (Ti and TiB₂ pre-reacted at 3400°F.) White areas are nickel, light grey areas are TiB₂, dark grey areas are TiO, and black area in center is an unidentified phase. Unetched.

Fig. 8. Microstructures of specimens made from titanium diboride plus 10 percent titanium and 30 percent nickel. X 1600

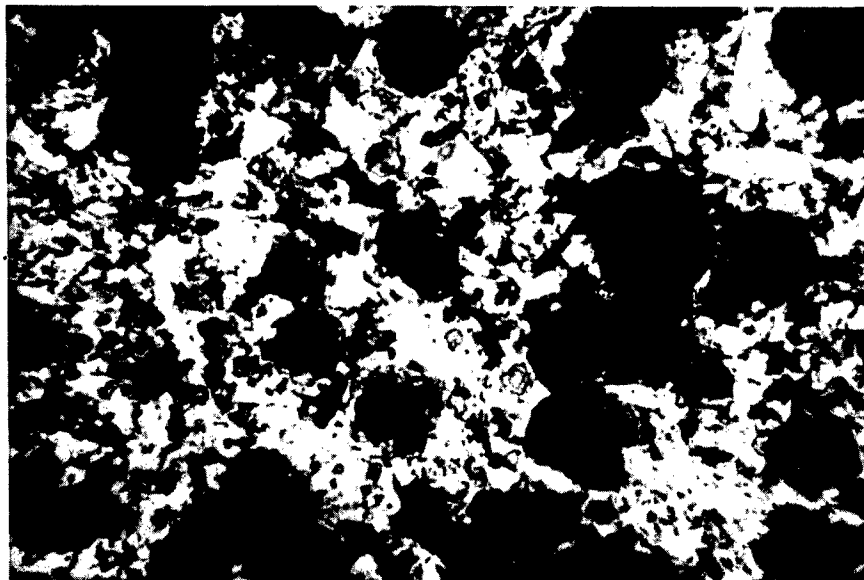


(a) Fired at 3400°F. Etched 10 min. in a solution consisting of 4 parts 48% HF, plus 2 parts conc. HNO_3 plus 94 parts methanol. Dark grey areas are TiO which seems to be more prevalent in regions where voids occur.

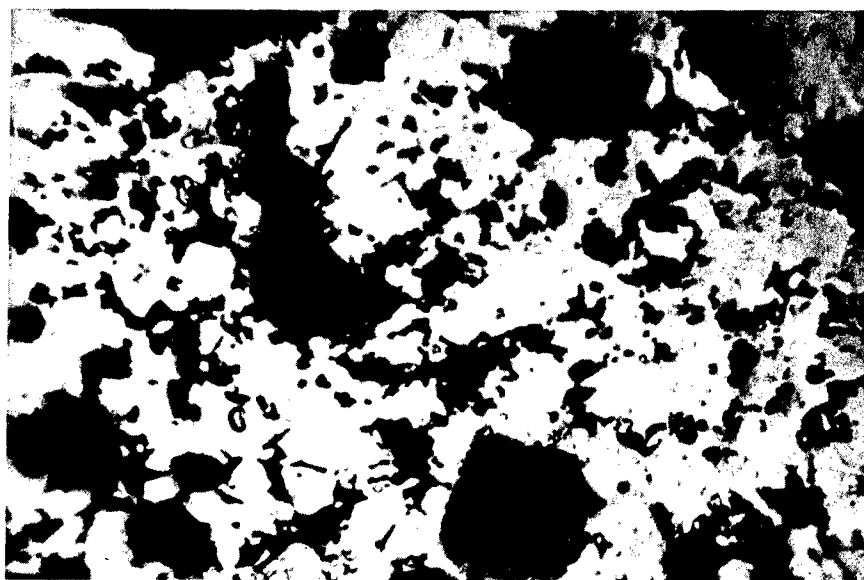


(b) Fired at 3500°F. (Ti and TiB_2 pre-reacted at 3400°F.) Light grey areas are TiB_2 and chromium. Dark grey areas in the center are TiO and black areas are voids. Unetched.

Fig. 9. Microstructures of specimens made from titanium diboride plus 10 percent titanium and 30 percent chromium. X 1000

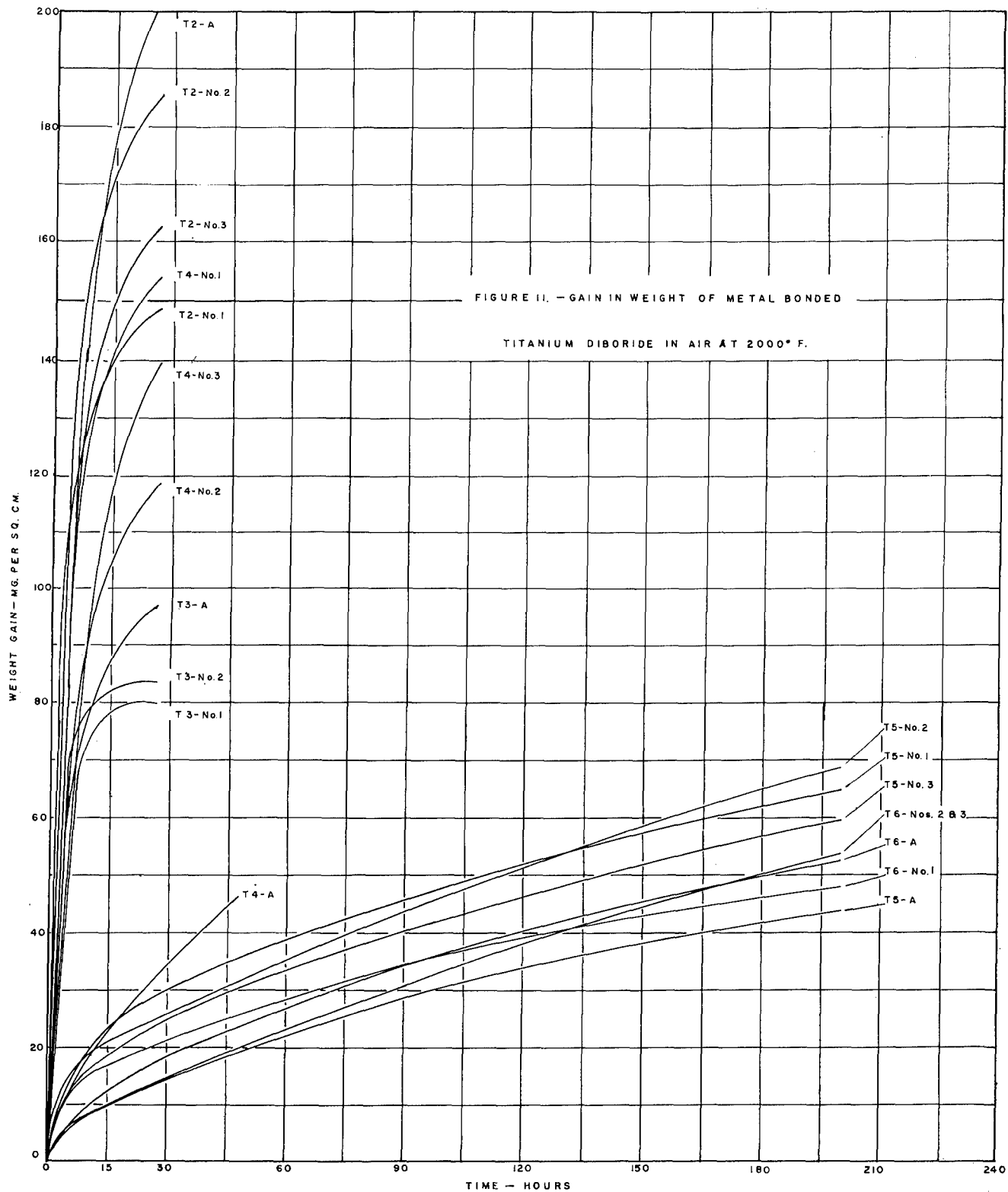


(a) Fired at 3700°F. Etched 10 min. in a solution consisting of 4 parts 48% HF plus 2 parts conc. HNO_3 plus 95 parts methanol.



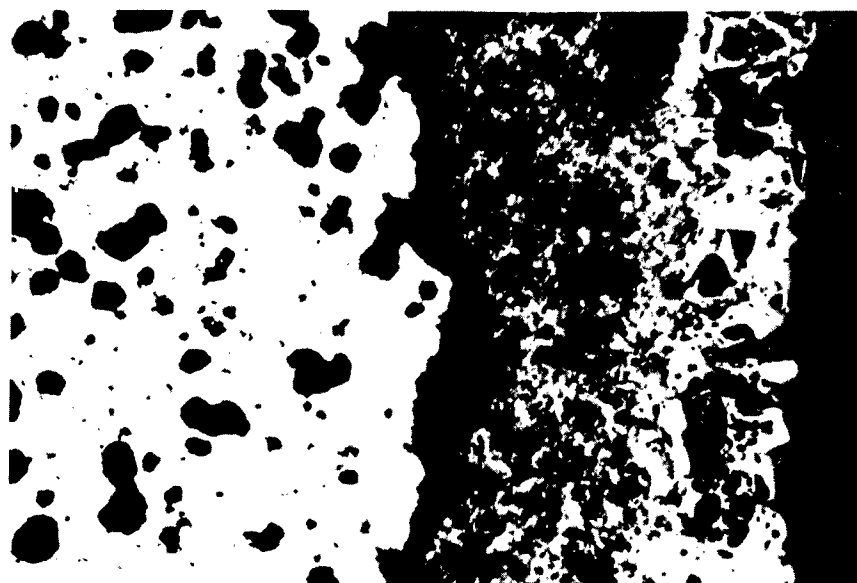
(b) Fired at 3600°F. (Ti and TiB_2 pre-reacted at 3400°F.) Black areas are voids. Dark grey areas are probably an oxide of zirconium. Unetched.

Fig. 10. Microstructures of specimens made from titanium diboride plus 10 percent titanium and 30 percent zirconium. X 1200



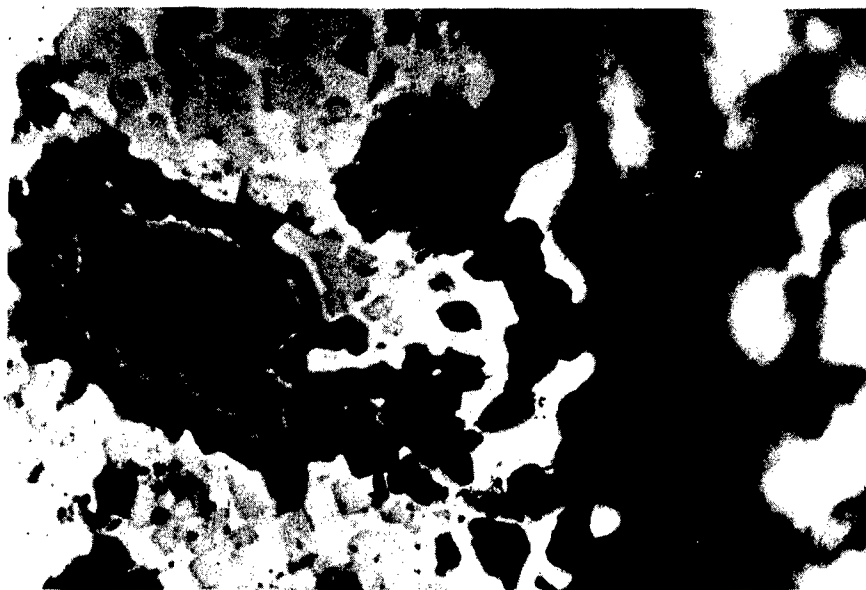


(a) Specimen containing nickel and initially fired at 3200°F. The oxide layer is between the white unoxidized body at the left and the black area on the extreme right which is lucite.

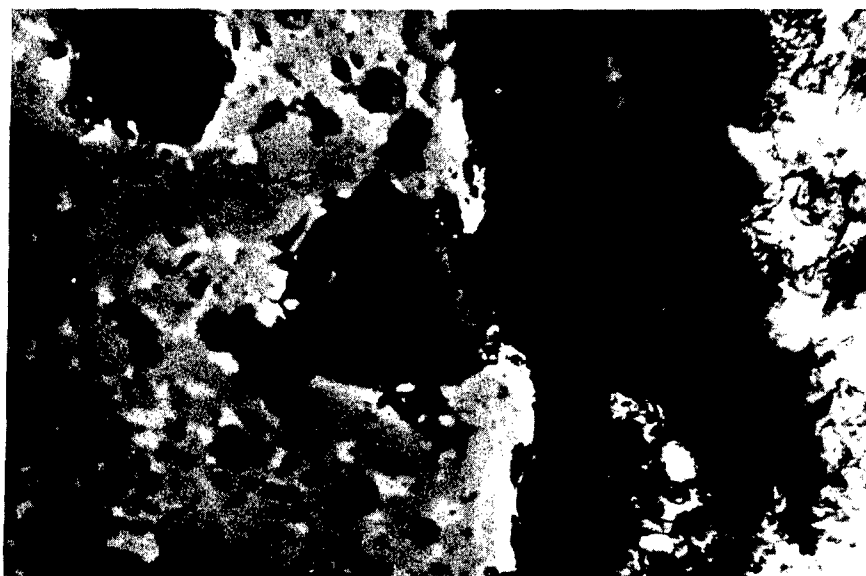


(b) Specimen containing chromium and initially fired at 3500°F. The oxide layer is between the white unoxidized body at the left and the black area on the extreme right which is lucite.

Fig. 12. Oxidation layer formed on specimens made from titanium diboride plus 10 percent titanium and 30 percent of either nickel or chromium. (Ti and TiB_2 pre-reacted at 3400°F.) Specimens heated in air for 200 hours at 2000°F. X 150



(a) Same specimen as shown in Fig. 12 (a).



(b) Same specimen as shown in Fig. 12 (b).

Fig. 13. Interface between unoxidized body and oxide layer.
X 1000. Oxide penetration is shown where voids occur in light
colored unoxidized body. Unetched.